

NOBEL LECTURE IN CHEMISTRY

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by

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INTRODUCTION

There is a well-known mathematical exercise called the Konigsberg Bridge Problem in which the solution involves crossing each of the city's bridges once and only once. When my wife and I first visited Stockholm together in April 1974, we had the distinct impression that our host, Paul Crutzen, was trying to illustrate the corresponding solution for Stockholm by leading us across every single bridge, on foot. We were in Stockholm because I had sent Paul a pre-print of our first scientific paper on the chlorofluorocarbon/stratospheric ozone problem [1], and he had invited me to present a lecture about this work to the Department of Meteorology of Stockholm University.

The starting point for that work was the discovery by Jim Lovelock that the molecule, CCl_3F , a substance for which no natural sources have been found, was present in the Earth's atmosphere in quantities roughly comparable to the total amount manufactured up to that date. Lovelock had earlier invented an extremely sensitive detection system employing electron capture (EC) by trace impurities, and attached it to the column of effluent gases from a gas chromatograph (GC), a device which separates a mixture of gases into its individual components. With this ECGC apparatus, Lovelock initially established that CCl_3F was always detectable in the atmosphere near his home in western Ireland, and then that it was also present in all of the air samples tested on the voyage of the R.V. Shackleton from England to Antarctica (Figure 1) [2]. The ECGC instrument is especially sensitive for CCl_3F , as well as for many other similar molecules in this chlorofluorocarbon class.

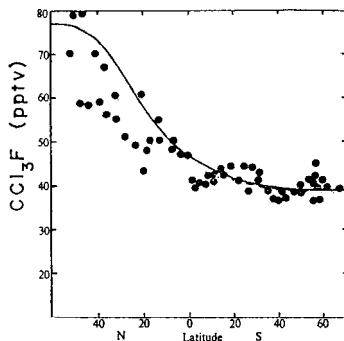


Figure (1). Mixing ratios of CCl_3F measured by James Lovelock [2] on board R. V. Shackleton in 1971.

The appearance in the atmosphere of a new, man-made molecule provided a scientific chemical challenge: Was enough known about the physico-chemical behavior under atmospheric conditions of molecules such as CCl_3F to allow prediction of its fate, once released into the environment? In 1973, I included in my yearly proposal to the U.S. Atomic Energy Commission, which had sponsored my research involving radioactive tracer species since 1956, a predictive study of the atmospheric chemistry of CCl_3F , in addition to the continuation of other studies already in progress. The A.E.C. agreed to permit this new venture, subject only to the requirement that I shift some of the funding already scheduled to be available for the studies on radioactivity.

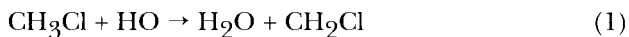
When Mario Molina joined my research group as a postdoctoral research associate later in 1973, he elected the chlorofluorocarbon problem among several offered to him, and we began the scientific search for the ultimate fate of such molecules. At the time, neither of us had any significant experience in treating chemical problems of the atmosphere, and each of us was now operating well away from our previous areas of expertise.

The search for any removal process which might affect CCl_3F began with the reactions which normally affect molecules released to the atmosphere at the surface of the Earth. Several well-established tropospheric sinks - chemical or physical removal processes in the lower atmosphere - exist for most molecules released at ground level:

(1) Colored species such as the green molecular chlorine, Cl_2 , absorb visible solar radiation, and break apart, or photodissociate, into individual atoms as the consequence;

(2) Highly polar molecules, such as hydrogen chloride, HCl , dissolve in raindrops to form hydrochloric acid, and are removed when the drops actually fall; and

(3) Almost all compounds containing carbon-hydrogen bonds, for example CH_3Cl , are oxidized in our oxygen-rich atmosphere, often by hydroxyl radical as in reaction (1).



However, CCl_3F and the other chlorofluorocarbons such as CCl_2F_2 and $\text{CCl}_2\text{FCClF}_2$ * are transparent to visible solar radiation and those wavelengths of ultraviolet (UV) radiation which penetrate to the lower atmosphere, are basically insoluble in water, and do not react with HO , O_2 , O_3 , or other oxidizing agents in the lower atmosphere. When all of these usual decomposition routes are closed, what happens to such survivor molecules?

* The chlorofluorocarbons (or CFCs) are often technically identified by a numerical formula which gives number of F atoms in the units digit, number of H atoms plus 1 in the tens digit, and number of C atoms minus 1 in the hundreds digit: $\text{CCl}_2\text{FCClF}_2 \rightarrow \text{CFC-113}$; $\text{CCl}_2\text{F} \rightarrow \text{CFC-11}$, dropping the 0 from 011; and $\text{CCl}_2\text{F}_2 \rightarrow \text{CFC-12}$. During the past decade the hydrogen-containing species have been distinguished from the fully-halogenated CFCs by subdivision into the two new categories of HCFCs (e.g. $\text{CHClF}_2 \rightarrow \text{HCFC-22}$) and HFCs (e.g. $\text{CH}_2\text{FCF}_3 \rightarrow \text{HFC-134A}$, with the A distinguishing this molecule from its isomer CHF_2CHF_3).

STRATOSPHERIC CHEMICAL PROCESSES

The radiation from the sun has wavelengths visible to humans from violet (400 nanometers, nm) to red (700 nm), plus invisible infrared (> 700 nm) and ultraviolet (< 400 nm) wavelengths. The energy of the radiation increases as the wavelengths shorten, and the absorption of highly energetic ultraviolet (UV) radiation usually causes the decomposition of simple atmospheric molecules.

All multi-atom compounds are capable of absorbing UV radiation if the wavelength is short enough, and almost all will decompose after absorbing the radiation. At the top of the atmosphere, the process is so rapid that a CFC molecule would last at most a few weeks if directly released there. However, CFC molecules in the lower atmosphere are protected against this very energetic UV radiation by O_2 and O_3 molecules at higher altitudes. In the upper atmosphere, the UV wavelengths below 242 nm can be absorbed by O_2 (Figure 2), splitting it into two oxygen atoms, as in equation (2). Each of

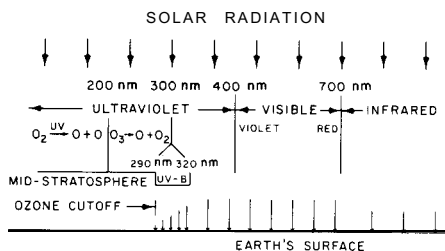
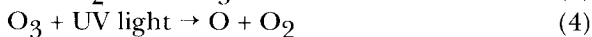


Figure (2) Solar spectrum, illustrating the absorption of ultraviolet radiation by O_2 and O_3 , and the location of the UV-B range between 290 nm and 320 nm. Ultraviolet radiation < 290 nm, "the ozone cutoff", does not reach the Earth's surface.

these O atom products normally adds to another O_2 molecule in (3) to form ozone, O_3 . Collision with some third molecule, M, is needed to stabilize the O_3 product. These ozone molecules in turn can absorb ultraviolet radiation in (4) and split off an O atom. Such absorption is especially strong for wavelengths shorter than 290 nm. Again, these O atoms usually reform ozone by reacting with O_2 .



Ozone is actually quite chemically reactive and sometimes intercepts the O atoms, as in (5). This set of four reactions involving O, O_2 and O_3 was already recognized by Chapman in 1930 [3].

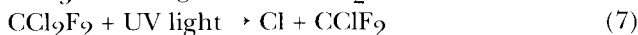
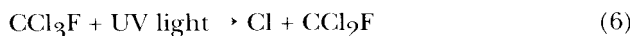


Through these processes, and others such as the free radical reactions of NO_x and ClO_x , described below, a balance of ozone is maintained in the atmosphere by which about 3 parts in 10^7 of the entire atmosphere are present as O_3 , versus almost 21% as O_2 . About 90% of these ozone molecules are

present at altitudes between 10 and 50 kilometers (km), i.e. in the stratosphere, where the mixing ratio of O_3 can rise as high as 1 part in 10^5 .

The solar UV energy absorbed in (4) is converted into heat by processes such as energy transfer to M in (3), providing a heat source in the 30-50 km altitude range. This heat source creates the stratosphere, the region between 15 and 50 km in which the temperature increases with altitude. The ozone layer thus performs two important physical processes: it removes short wavelength UV radiation, and changes this energy into heat, both creating and maintaining the stratosphere.

Because both O_2 and O_3 can absorb short wavelength UV radiation, no solar radiation with wavelengths < 290 nm penetrates below the stratosphere. The CCl_3F molecule was known from laboratory studies to be able to absorb UV radiation at wavelengths < 220 nm, but to encounter such solar radiation in the atmosphere the molecule must first drift randomly through the atmosphere to altitudes higher than most of the O_2 and O_3 molecules - roughly to 25 or 30 km. More than 98% of the atmosphere and 80% of the ozone lies below 30 km altitude. In this rarefied air, the CFC molecules are exposed to very short wavelength UV radiation and decompose with the release of Cl atoms, as in (6) and (7). Because at any given time, only a very small fraction of CFC molecules are found at altitudes of 30 km or higher, the average molecule survives for many decades before it is decomposed by solar UV radiation.



In 1974, we calculated the vertical profile to be expected for CCl_3F in the stratosphere, using several different sets of eddy diffusion coefficients, the parameter used to simulate vertical motions in these calculations [4]. The resulting vertical profiles for CCl_3F are all quite similar, as illustrated in Figure 3, because the decomposition rate for this molecule escalates rapidly with increasing altitude in the 20-30 km range. With each of these parameters, the estimated average lifetime in the atmosphere for CCl_3F was in the range from 40 to 55 years, and others extended the lifetime to 75 years. The range of lifetimes calculated for CCl_2F_2 was 75 to 150 years [1,4].

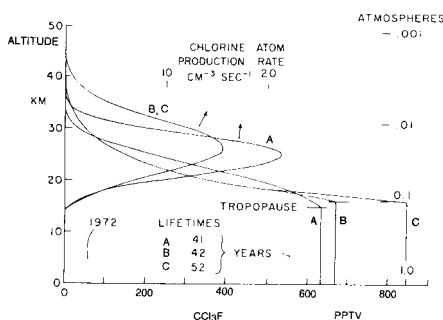
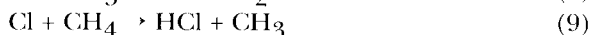


Figure (3) Vertical profiles of CCl_3F in pptv (parts per trillion by volume) at steady state, as calculated for three different diffusion models (A, B, C) and 1972 emission rate [4]. The peak photolytic destruction of CCl_3F occurs at an altitude of 28 kilometers.

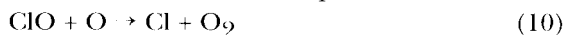
The answer to our original scientific question is that the eventual fate of the CFC molecules is photodissociation in the mid-stratosphere with the release of atomic chlorine, but on a time scale of many decades. What is the fate of these chlorine atoms at an altitude of 30 km?

CHLORINE CHEMISTRY IN THE STRATOSPHERE

The major chemical components of the mid-stratosphere are well known, and their reaction rate constants with atomic Cl have been measured in the laboratory. By combining these data, the conclusion is readily reached that almost all chlorine atoms react with ozone by (8), forming another reactive molecule, ClO. This probability is about 1000 times more likely than reaction with methane, as in (9). The questions of the ultimate sinks, first for CCl_3F and then for Cl, have thus been answered, and the question now moves to a third molecule, the ClO product from (8): What happens to ClO at 30 km?



Two important answers appear: reaction with O atoms in (10) or with NO in (11). The combination of reactions (8) and (10) sums to the equivalent of (5), and constitutes a free radical catalytic chain reaction in which the Cl atom alternates among the chemical species Cl and ClO. The first step removes one O_3 molecule, while the second intercepts an O atom which could have become an O_3 by (3), but is instead also converted to O_2 . The Cl atom, however, is only a catalyst, and remains to initiate the process once more.



This Cl/ClO cycle can be repeated hundreds or thousands of times, converting back to molecular O_2 in each pair of reactions one ozone molecule and one oxygen atom. When this catalytic efficiency of about 100,000 ozone molecules removed per chlorine atom is coupled with the yearly release to the atmosphere of about one million tons of CFC's, the original question chiefly of scientific interest has now been converted into a very significant global environmental problem - the depletion of stratospheric ozone by the chlorine contained in the chlorofluorocarbons.

The ClO_x chain of reactions (8) and (10) was discovered earlier in 1973 by Stolarki and Cicerone, who were interested in the possible natural release of HCl to the atmosphere from volcanoes, or of man-made chlorine in the exhaust of the rockets scheduled for propulsion of the space shuttle [5]. The ClO_x chain has a close analogy with the NO_x free radical catalytic chain of reactions (12) and (13), which also combine to convert O and O_3 into two molecules of O_2 . This chain can be initiated in the stratosphere by the decomposition of the long-lived molecule nitrous oxide, N_2O [6]. Alternatively, the NO_x chain can also be triggered by the direct release of NO and NO_2 in the exhaust of high-flying aircraft [7, 8]. The potential effects on stratospheric ozone of NO_x from supersonic transport aircraft

such as the Concorde and the proposed Boeing aircraft were discussed in detail during the period 1971 to 1974 under the Climatic Impact Assessment Program [9, 10].



Reactions such as (9), (11) and (14) show that the distribution of chlorine is closely intertwined with the concentrations of other stratospheric species, including the nitrogen oxides, methane, and oxides of hydrogen. The most significant homogeneous gas phase interconnections among the active chain species (Cl, ClO) and the reservoir molecules (HCl, HOCl, ClONO₂) in the tropic and temperate zone stratosphere are shown in Figure 4. Because of the large-scale mixing processes which dominate throughout the troposphere and stratosphere, the total mixing ratio of Cl from any species released at the Earth's surface is essentially constant versus altitude. However, the fraction in each of the various chlorine-containing chemical forms varies significantly with altitude (Figure 5).

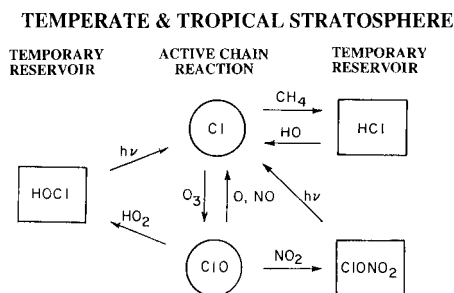


Figure (4) The most important stratospheric chemical transformations among inorganic chlorine species, except during the polar winter. Ozone depletion occurs only while chlorine is in the forms of Cl and ClO.

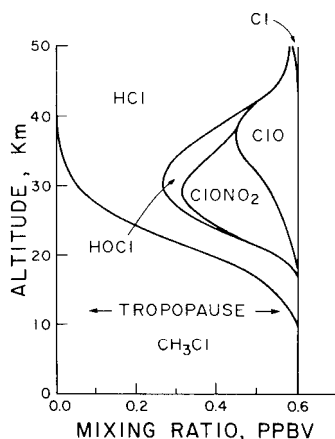


Figure (5) Schematic illustration of the distribution of chlorine among various chemical forms after release to the atmosphere in the form of methyl chloride (CH₃Cl). At steady state, the sum of the mixing ratios at all altitudes is constant, equal to the tropospheric mixing ratios of CH₃Cl alone.

Our original calculations about the behavior of the CFC species in the stratosphere were actually predictions of the vertical distribution because no measurements were then available for any chlorinated species in the stratosphere, and certainly not for the CFCs. During 1975, two different research groups sent evacuated containers equipped with pressure-sensitive valves up on high altitude balloons, and recovered air samples from the stratosphere. The measured mixing ratios for CCl_3F (Figure 6) were in excellent agreement with the vertical profiles calculated by us in the previous year. This fit between theory and experiment demonstrates both that CFCs reach the stratosphere and that they are decomposed there by solar ultraviolet radiation at the altitudes predicted earlier [11,12].

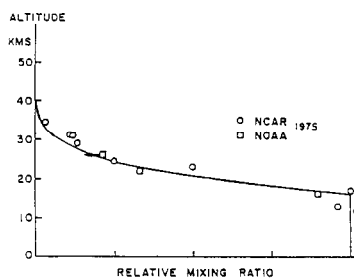


Figure (6) Mixing ratios for CCl_3F observed in 1975 by research groups from NCAR (o) [12] and NOAA (□) [11] normalized to tropospheric value as 1.0. The solid line is the calculated value with diffusion coefficient C in Figure 3 [4].

GROWTH OF TROPOSPHERIC CFC CONCENTRATIONS

When upward transport of the CFCs into the stratosphere proved to move at the same rate as for all other molecules, attention returned to the possibility of tropospheric sinks. The rapid tropospheric removal processes (photolysis, rainout, oxidation) were readily eliminated. Nevertheless, the calculated 50 to 100 year lifetimes for the various CFCs left room for concern about the possibility of an accumulation of minor sinks, or even an undiscovered tropospheric sink. While atmospheric and laboratory tests can be conducted appropriate to each proposed individual sink, an even more comprehensive approach is the measurement of the sum for all tropospheric removal processes, including those not yet specifically identified. This can be accomplished by measurement of the actual lifetime of the CFCs in the atmosphere itself, and requires accurate knowledge both of the amounts of a particular CFC released to the atmosphere and of the amount still there.

An electron capture gas chromatographic trace, taken by the same technique originally developed by Lovelock, is shown in Figure 7 for an air sample collected in Tokyo in 1989. Tokyo is not unusual. Similar high concentrations are found in all major cities because most of the technological uses of CFCs take place in urban areas. While this is an accurate assessment of the halocarbon impurities found in Tokyo air on that date, it is not very useful

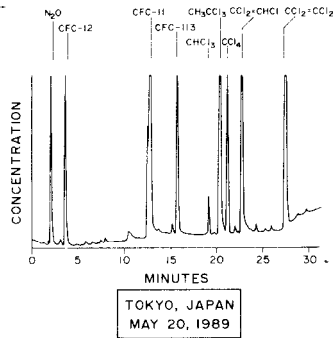


Figure (7) Analysis by electron capture gas chromatography of a Tokyo air sample collected on May 20, 1989. Four of the peaks rise above the printed scale values. The detector has a different response for each compound, requiring calibration for each.

for a global assesment of total CFC concentrations because the measurement is not representative of the whole atmosphere.

The air volume associated with cities, and the amounts of CFCs in that air, represent minuscule fractions of the total atmosphere, and of its total CFC content. Instead, what is required are measurements at enough representative remote locations to permit a global assay. A comparable electron capture display from an air sample collected a few miles from Barrow, Alaska, (71 °N Latitude) in 1989 is shown in Figure 8. Although the amounts are certainly smaller, the three major CFC molecules are all clearly present near Barrow. Many of the other molecules found in Tokyo (Figure 7) have atmospheric lifetimes of one year or less, and are detected only in very low concentration or not at all in northern Alaska.

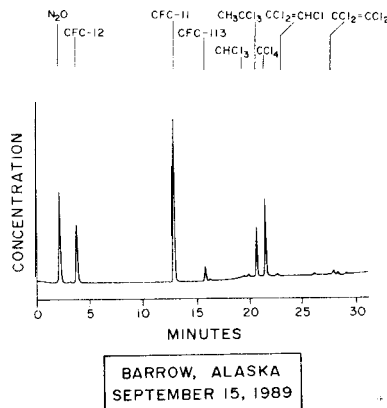


Figure (8) Analysis by electron capture gas chromatography of an air sample collected in Barrow, Alaska, on Sept. 15, 1989. The detector has a different response for each compound, requiring calibration for each.

The west-east global mixing processes across longitudinal lines are sufficiently rapid that good estimates can be obtained for molecules as long-lived as the CFCs from a set of air samples collected within a short time period from remote locations across most of the north-south latitudinal spread. The

CCl_3F concentrations found at such a set of remote locations are illustrated in Figure 9 for the summer of 1979, and in Figure 10 for December 1987. Both of these figures illustrate that north-south mixing is quite rapid in the atmosphere, for the gradient from north-to-south is only about 10%, despite the release of about 95% of CCl_3F in the northern hemisphere, mostly between 30°N and 60°N latitudes. The average time for a molecule to mix from the northern to southern hemisphere, or vice versa, has been calculated from the release patterns in comparison with these measured concentrations and is approximately 15 months. The average CFC molecule therefore mixes back and forth between the northern and southern hemispheres 20 to 40 times or more before its ultimate decomposition in the stratosphere. Only the continued injection of CFC_3 into the northern hemisphere maintained the observed N/S concentration gradient from 1971 into the late 1980s.

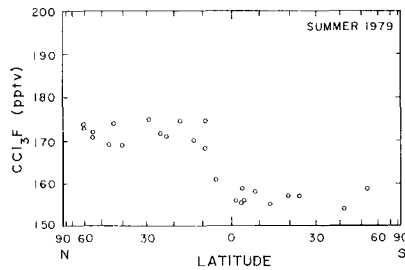


Figure (9) Mixing ratios of CCl_3F in parts per 10^{12} versus latitude, as measured at remote sites in 1979.

Comparison of the data in Figures 9 and 10 with the Lovelock data demonstrates that the northern hemisphere concentration of CCl_3F increased from about 70 parts per trillion by volume ($\text{pptv} = 10^{-12}$) in 1971 to 170 pptv in 1979 and 250 pptv in 1987. This steady increase in concentration with time is precisely what is expected for a molecule with an atmospheric lifetime in the 50 to 100 year range. In 1995, the best estimate for these CFC lifetimes made from a comparison of total atmospheric burden versus total release is 50 years for CCl_3F and 102 years for CCl_2F_2 [13]. Both estimates are well within the ranges of lifetimes calculated 20 years earlier [1,4]. This close agree-

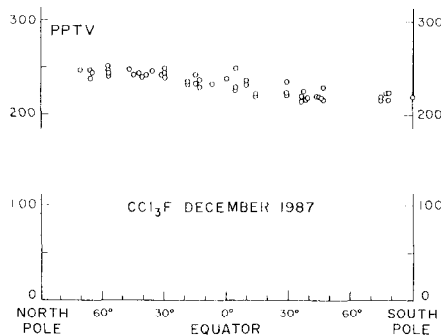


Figure (10) Mixing ratios of CCl_3F in parts per 10^{12} versus latitude, as measured at remote sites in December 1987.

ment between measured lifetimes and those calculated on the assumption that no important tropospheric loss processes exist is a clear indication that this assumption is correct. The ultimate fate for the CFC compounds lies in their solar ultraviolet photodissociation in the mid-stratosphere.

A typical measurement with the current version of our analytical system for chlorocarbon molecules is shown in Figure 11 for an air sample collected through an external air intake on a C-130 Hercules aircraft 850 miles south of New Zealand on November 15, 1995. Even in this remote location, sixteen different low molecular weight compounds containing Cl or Br atoms are readily detected (Figure 11), together with others such as $O=C=S$ and N_2O (not shown), the molecule whose atmospheric chemistry was considered by Crutzen 25 years ago [6].

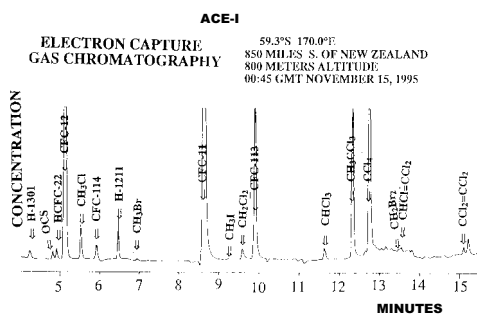


Figure (11) Electron capture gas chromatography of an air sample collected with an aircraft south of New Zealand on November 15, 1995.

SPRINGTIME LOSS OF OZONE IN THE ANTARCTIC

The greatest surprise in the CFC-ozone story was revealed in the spring of 1985, with the discovery by Joe Farman and his colleagues from the British Antarctic Survey of massive springtime losses of ozone over their station at Halley Bay, Antarctica ($75.5^{\circ}S$ Latitude) [14]. This station was established in preparation for the International Geophysical Year of 1957-1958, and was equipped with a Dobson ultraviolet spectrometer for the measurement of total ozone. The principle of this instrument, designed by Dobson in the 1920's, relies on the measurement at the surface of the Earth of the ratio of received solar radiation for two UV wavelengths. One of these is moderately absorbed by ozone, and one is almost unaffected by ozone, as illustrated in Figure 12. A typical wavelength pair is the C pair which uses 311.45 nm for the former, and 332.4 nm for the latter.

While the absorbing characteristics of most molecules vary continuously with wavelength, the ultraviolet region is often divided for convenience in description into three arbitrary wavelength regions: UV-A, 400 nm to 320 nm, most of which reaches the Earth's surface; UV-B, 320 nm to 290 nm, for which some reaches the surface; UV-C, < 290 nm, of which none reaches the surface. The various wavelength pairs used with a Dobson spectrometer usu-

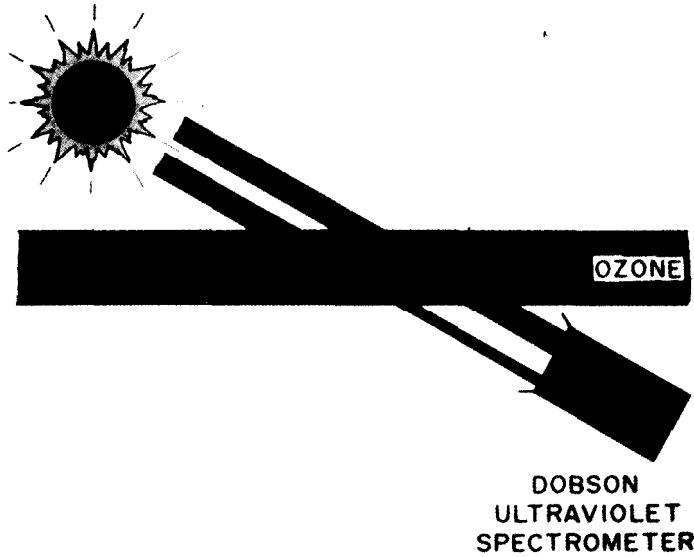


Figure (12) Standard technique for measurement of ozone with a Dobson spectrometer. The ratio of the two UV wavelengths is dependent upon the ozone content of the atmosphere and the solar zenith angle.

ally compare one UV-B wavelength against one from the UV-A range. Most concerns about UV effects on biology are directed toward the UV-B range because UV-C radiation doesn't get down to the levels where biological species flourish, and UV-A radiation at the surface is so intense that species without some mechanism for dealing with UV-A would long since have become extinct.

In the northern hemisphere, the highest total ozone concentrations are observed in the polar regions around the spring equinox (i.e. March/April), as shown in Figure 13. (The technical unit used to measure total ozone is the

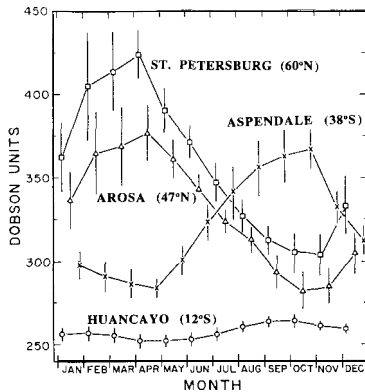


Figure (13) Seasonal variation of ozone concentrations as measured with a Dobson spectrometer for two northern hemispheric stations (St. Petersburg, Russia; Arosa, Switzerland), one tropical station (Huancayo, Peru), and one southern hemispheric station (Aspendale, Australia). The vertical bars indicate the natural variability of ozone measurements for that location and that calendar month. One Dobson Unit is one millimeter-atmosphere-centimeter and is approximately one part in 10⁹ by volume.

milliatmosphere centimeter, but this has been almost universally superseded by its other name, the Dobson Unit, D.U. The Dobson unit represents approximately 1 part in 10^9 of the atmospheric molecules by volume, and the average global concentration is about 300 D.U.) The spring maximum values are higher at the higher latitudes, as at St. Petersburg, Russia, versus Arosa, Switzerland, while the highest of all are found in the north polar region. On the other hand, tropical locations have the lowest year-round levels of ozone, with little seasonal variation, as illustrated for Huancayo, Peru.

With no significant prior information about Antarctic meteorology in 1956, Dobson anticipated finding a spring equinoctial maximum over Halley Bay similar to that previously observed at Spitzbergen, Norway. However, instead of increasing steadily through the autumn and winter, as observed in the north, the southern polar ozone values remained essentially constant through the autumn and winter darkness, and into mid-spring. They then increased sharply to a peak in mid-November, as illustrated in Figure 14 for the summers of 1956-57, 1957-58 and 1958-59 [15]. Dobson recognized that this represented the discovery of a very strong Antarctic polar vortex, which prevented until its breakdown in mid-spring, the arrival over the polar regions of ozone-richer stratospheric air from the temperate zone.

This pattern of level ozone values into mid-spring was observed through-

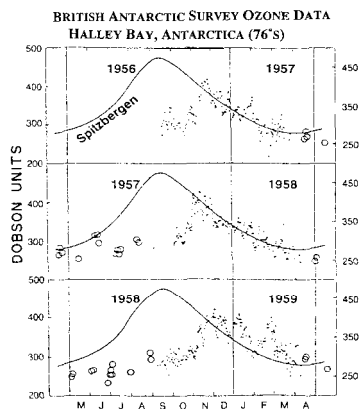


Figure (14) Daily ozone measurements at Halley Bay, Antarctica, during 1956-1959, in comparison with the pattern previously observed in the north polar region at Spitzbergen, Norway [15]. Dots indicate data using the sun as the UV source, and the less accurate circles with the moon as the source. Vertical scale: ozone in Dobson units.

out the 1960's and early 1970's. However, in the late 1970's, the average October ozone values over Halley Bay began to decrease, dropping below 200 D.U. in 1984 versus the 300 to 320 D.U. values of the 1960's (Figure 15). These data were reported in May 1985, together with the hypothesis that the ozone decrease was correlated with the increasing CFC concentrations in the atmosphere [14]. This loss of ozone begins soon after the end of the polar winter darkness, and proceeds very rapidly for the next six or seven weeks into mid-October.

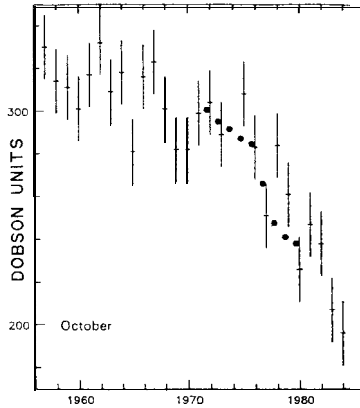


Figure (15) Average ozone concentrations in Dobson units for the month of October, 1957-1984, Halley Bay, Antarctica [14]. The black dots indicate on a relative scale the concentrations of CCl₄F versus time, plotted downward from zero at the top.

These observations of substantially less ozone over Halley Bay in October in the 1980's were quickly shown to be characteristic of the entire south polar region by the measurements of the TOMS (Total Ozone Mapping Spectrometer) on the Nimbus-7 satellite [16]. This instrument also measures ozone from the ratio of two UV wavelengths, utilizing solar UV back-scattered from the troposphere through the stratosphere. More than 100,000 daily TOMS ozone measurements over the entire Southern hemisphere are expressed in Figure 16 through a color code for one early October day each in 1979, 1983, 1987 and 1992. In these TOMS displays, the lowest

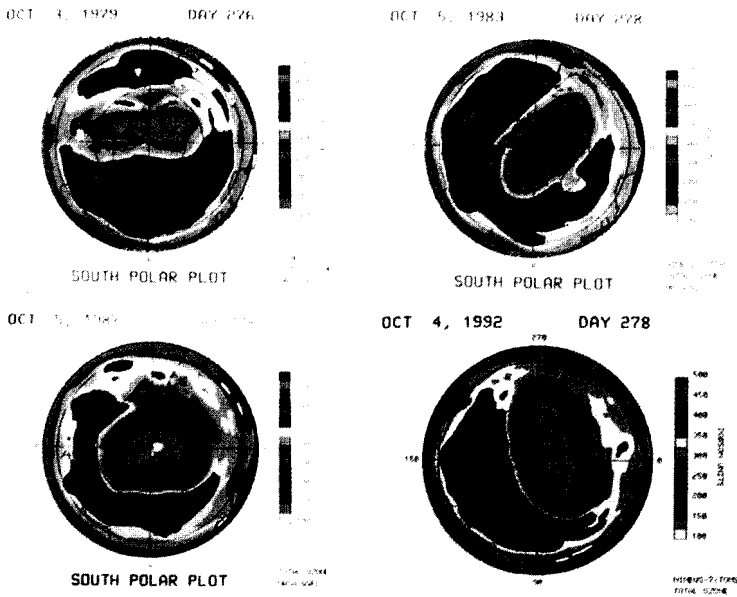


Figure (16) Southern hemispheric total ozone concentrations measured with the TOMS (Total Ozone Mapping Spectrometer) on the Nimbus 7 satellite: (a) October 3, 1979; (b) October 5, 1983; (c) October 5, 1987; (d) October 4, 1992. The color code for the measured numerical values is given to the right.

October ozone values fell rapidly from 250 D.U. to 175 D.U. and then 125 D.U. between 1979 and 1987. The ozone loss is not confined to the central area, as shown in Figure 16, with substantial reductions by 1983 in the areas originally covered by 450-500 D.U. in 1979. A totally different kind of ozone measurement, utilizing its chemical capability for oxidizing iodide ion to elemental iodine, was used on balloon sondes, demonstrating that most of this ozone loss occurred in the lower stratosphere (Figure 17). Again, the loss of ozone has been observed to be very rapid between late August and October.

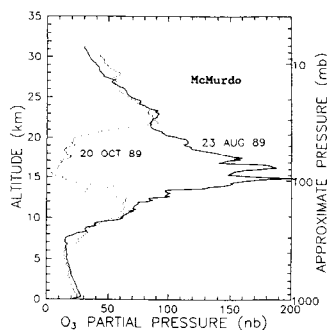


Figure (17) Partial pressures of ozone in nanobars versus altitude, as measured by balloon sondes from McMurdo, Antarctica. Solid line: August 23, 1989, in late winter at the end of the polar night. Dotted line: October 20, 1989, after two months of sunlight.

CHEMISTRY OF THE POLAR STRATOSPHERE

Numerous theories were suggested for this new observation of ozone loss, and can generally be classified into three groups: (a) natural change in the dynamics of the Antarctic stratosphere; (b) change in the natural chemistry, e.g. NO_x of the stratosphere; or (c) chemical changes induced by mankind, especially through the introduction of artificial chlorine-containing compounds such as the CFCs. A decrease in the springtime stratospheric temperatures was observed to accompany the observations of lessened quantities of ozone, and was briefly considered as a possible cause for its destruction [17]. However, the lowered temperatures were soon established to be occurring after the ozone loss, and to be the consequence of reduced UV absorption by reduced amounts of ozone, not a cause of the ozone loss. The observed temperature decreases are in fact a slower warm-up from the wintertime temperature minimum.

Three polar expeditions in 1986 and 1987 provided the scientific basis for the conclusion that the ozone losses over Antarctica were indeed the consequence of chemical reactions driven by the much higher stratospheric chlorine concentrations of the mid-1980's versus those of 1950-1970. Two of these were ground-based expeditions to McMurdo, Antarctica, led by Susan Solomon. Two maxima were detected in 1986 in the vertical profile of the important free radical, ClO, by ground-based millimeter wave spectroscopy [18]. The larger maximum in ClO concentrations was found in the lower

stratosphere, reaching ppbv (10^9) concentrations, and coincident with the altitudes of major ozone loss. These results were then followed in 1987 by in situ measurements of ClO and O_3 within the polar vortex by instruments on the high-flying ER-2 aircraft [19]. These aircraft experiments were carried out from a base in Punta Arenas, Chile (53°S Latitude), and entered the polar vortex over the Antarctic peninsula. The data of Jim Anderson showed clearly (Figure 18) on the first successful flight on August 23 the ppbv levels of ClO over Antarctica. However, the simultaneous ER-2 data for ozone showed little or no change in concentration inside or outside the polar vortex. At this late-winter date, sunlight had only been available in the Antarctic stratosphere for a few days. In contrast, 24 days later on September 16, the ClO levels over Antarctica were again in the ppbv range, but this time approximately two-thirds of the ozone within the polar vortex had already disappeared. The edge of the Antarctic polar vortex was particularly ill-formed on September 16, and the high values of ClO and low values of O_3 tracked each other in perfect anti-coordination (Figure 18).

The chlorine chemistry of the lower Antarctic stratosphere has some substantial differences from that of the upper stratosphere in the temperate and tropical zones. Because the concentration of O atoms is very low in the polar lower stratosphere, reaction (10) is quite slow and the ClO_x chain of (8) + (10) is no longer effective. At these altitudes, the winter temperatures drop to the -80°C range, low enough for the formation there of polar stratospheric clouds (PSCs) which can contain both HNO_3 and H_2O [20-22]. Such low temperatures, and the accompanying clouds, are not generally found in the temperate zone stratosphere. However, the same air remains trapped in the strong Antarctic polar vortex throughout the total winter darkness, and the temperatures drop low enough for cloud formation.

These polar clouds furnish active surfaces on which chemical reactions can occur, including reactions such as (15) and (16) involving reservoir molecules HCl and ClONO_2 [23-26]. The products Cl_2 and HOCl are released from the PSC surface back into the gas phase, where they are photo-

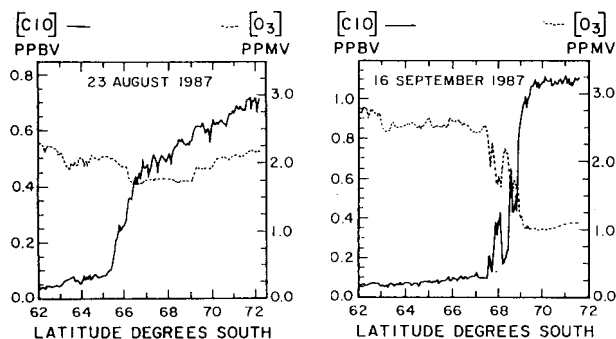
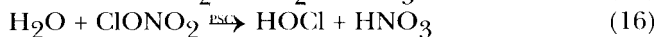
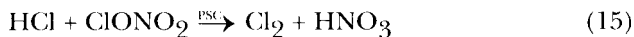
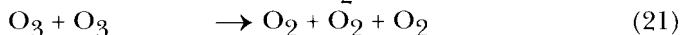
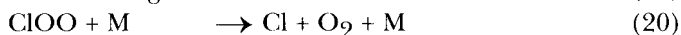
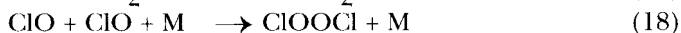
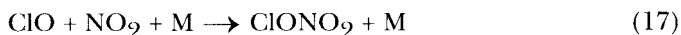


Figure (18) Chlorine oxide (—) and ozone (···) measurements with the ER-2 aircraft on flights from Punta Arenas, Chile, over Antarctica [19]. Left: August 23, 1987; Right: September 16, 1987.

lyzed when the sun returns from its months-long absence. The HNO_3 from such reactions remains in these clouds, tending to denitrify the air mass. When cold enough, sufficient water molecules can also add to the PSC particles to make them fall by gravitation, tending to dehydrate the air mass as well.



An important aspect of the denitrification process is the very low residual concentration of NO and NO_2 , with the absence of the latter severely curtailing the formation reaction for chlorine nitrate by (17). Without this removal process for ClO radicals, the ClO concentrations rise to mixing ratios in the ppbv range, and begin to react in significant numbers with other ClO radicals to form Cl_2O_2 by (18) [27]. The chlorine oxide dimer, ClOOCl , can then be destroyed by sunlight in (19), releasing one Cl atom each in (19) and (20). The sum of reactions [8] + [8] + [18] + [19] + [20] sums to [21] by which two O_3 molecules are transformed into three O_2 molecules. This alternate polar ClO_x chain reaction converts ozone into molecular O_2 without the need for the O atom step of reaction (10). Other reactions involving Br atoms from Halon molecules such as CBrF_3 and CBrClF_2 or methyl bromide (CH_3Br) are exceedingly efficient in removing ozone as well.



OZONE LOSSES IN THE NORTHERN TEMPERATE ZONE

In 1985, the several existing statistical evaluations of the combined data from the Dobson stations in the northern hemisphere appeared to indicate that no significant loss in total ozone had occurred there [28]. The longest series of these ozone measurements without any significant breaks has been carried out since August 1931 in the Swiss alpine community of Arosa. In 1986, Neil Harris and I began a reexamination of the Arosa data series, treating it not as a single comprehensive set, but as a collection of twelve separate data sets, one for each calendar month. Interannual ozone comparisons show in Figure 13 substantial seasonal differences in the variability of the monthly averages. While each year individually shows the normal north temperate zone pattern of maximum ozone values around the spring equinox, and a minimum at the beginning of autumn, the year-to-year variability in average ozone concentration for each month is much greater for the January-to-April

period than it is for July-to-October. When this 56-year data series from Arosa was broken into two periods - the 39 year period from 1931-1969, and the 17-year period from 1970-1986-the interesting result emerged that significantly less ozone was measured for several of the autumn-winter months after 1970 than in the previous four decades [29]. Figure 19 shows this Arosa wintertime ozone loss after the inclusion of data from 1987-88.

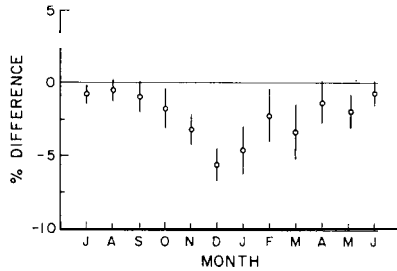


Figure (19) Changes in monthly average total ozone concentrations measured with a Dobson spectrometer at Arosa, Switzerland, for 1970-1988 versus 1931-1969 [Updated from 29]. Negative values represent smaller average concentrations after 1970.

We then extended this inquiry to two U.S. ozone stations, Caribou (Maine) and Bismarck (North Dakota), and found that these two also exhibited wintertime losses when the data for 1965-1975 were compared with 1976-1986 [29]. This comparison of consecutive 11-year periods corresponding minimizes any influence of variations in UV emission corresponding to the 11-year solar cycle on the evaluation of the long term trends. Subsequently, the WMO/NASA Ozone Trends Panel confirmed (Figure 20)

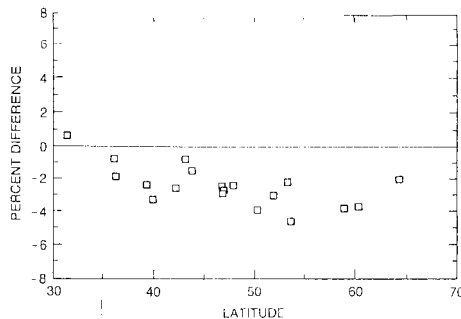


Figure (20) Changes in average "winter" season (DJFM) total ozone concentrations, 1976-1986 versus 1965-1975 for all Dobson stations north of 30° North Latitude with a complete 22 year (two complete solar cycles) record, 1965-1986 [30]. Negative values represent smaller average concentrations after 1975.

that all 18 of the ozone stations between 35°N and 60°N Latitudes with at least 22 years of data (i.e. also covering two complete 11-year solar cycles) had less wintertime ozone in 1976-1986 than in the earlier period [30]. An earlier National Academy of Sciences/National Research Council report had concluded that loss of ozone had already occurred at the altitudes between 35 and 40 km for which the ClO_x chain reaction of (8) + (10) was predicted to be most effective [31]. However, the Ozone Trends Panel

report was the first assessment document to assert that significant ozone loss had, already been observed over the highly-populated areas of North America, Europe, the Soviet Union and Japan. The combination of very large springtime losses of ozone over Antarctica directly attributable to man-made chlorine compounds introduced into the stratosphere, and measurable ozone losses in the north temperate zone, brought a rapid change in the attitudes of CFC-producers and many of the users, and a complete phaseout of CFC production and uses became a widely accepted goal.

THE MONTREAL PROTOCOL FOR REGULATION OF CFCs

Regulations for the control of CFC emissions had first been introduced during the late 1970s for the use of CFC-11 and CFC-12 as propellant gases for aerosol sprays, but only in the United States, Canada, Sweden and Norway. In 1985, a United Nations meeting in Vienna, Austria, had agreed to a convention concerning protection of the stratospheric ozone layer. Then, in September 1987, a further agreement, known as the Montreal Protocol, called for actual limitations on the emissions of CFCs, with a 50% cutback in CFC production scheduled by the end of the century [32]. The terms of the Montreal Protocol called for periodic revisits to the controls, and a meeting in London in 1990 changed the restricted production into an outright phaseout of CFCs by the year 2000. A further meeting in Copenhagen in 1992 accelerated the phaseout to Jan. 1, 1996, for the major industrial countries, and included compounds such as methylchloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), and the bromine-containing halons, i.e. H-1301 (CBrF_3), H-1211 (CBrClF_2), H-2402 ($\text{CBrF}_2\text{CBrF}_2$).

CHANGES IN ULTRAVIOLET FLUX AT EARTH'S SURFACE

Most of the measurements of total ozone, including the Dobson and TOMS data, actually depend upon the ratio of two wavelengths of solar ultraviolet radiation, as described earlier. A change in the amount of ozone along the path of the UV radiation is inferred from a change in the wavelength quality of the detected radiation. In these cases, the existence of a correlation between ozone and UV-B radiation under clear-sky conditions is a tautology. Less reported ozone means either more UV-B or less UV-A or both, and no mechanisms for significant changes in UV-A radiation have been put forward. However, because actual well-calibrated, precision absolute measurements of ultraviolet radiation over multi-decadal periods of time do not exist, no long-term comparison of trends in ozone concentrations and UV-B radiation has been possible.

In the past decade, instruments capable of such ultraviolet measurements have been deployed in various locations, especially in the south polar region, including three Antarctic stations - South Pole, McMurdo (78°S), and Palmer (64°S)—as well as Ushuaia, Argentina (55°S). Because the

Antarctic polar vortex, and its low ozone concentrations during recent Octobers, can be very elongated (See Figure 16, for Oct. 4, 1992), the possibility now exists for much higher UVB exposures in the southern high latitudes than in previous times.

Comparison of the measured UV-B intensities for the same solar zenith angle in spring (i.e., depleted ozone) and autumn (relatively normal ozone) allow an experimental confirmation of the anticipated anti-correlation between UV-B and total ozone. The measured correlation in Figure 21 for the

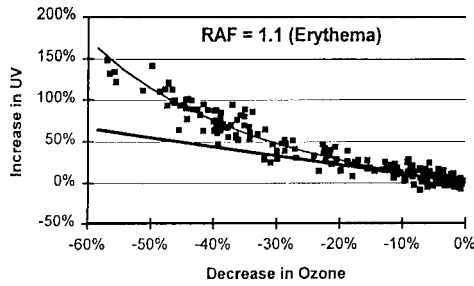


Figure (21) Percentage increases in UV-B radiation (erythemally weighted) versus percentage decreases in total ozone, at the South Pole, 1991–1992 [33].

South pole in 1991-1992 shows a 150% increase in UV-B for a 50% decrease in ozone content [33]. Furthermore, on October 26, 1993, when a particularly low ozone value existed over Palmer in the Antarctic peninsula, the UV-B intensity exceeded by 25% the highest intensity recorded in San Diego, California, for any day of 1993, the most intense there being June 21, 1993 [34]. The remarkable further observation was also recorded that the most intense weekly UV-B exposure in any single week at any of these stations was recorded at the South Pole. There, even though the sun is low on the horizon, the very low concentrations of ozone in the late Antarctic spring, the general absence of clouds, and the 24 hours per day of continuous sunlight combined to permit a higher weekly dose of UV-B than in any week in San Diego, California [34]. The often-heard statement that UV-B intensities in

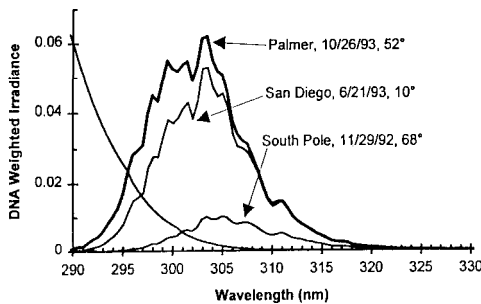


Figure (22) Maximum UV-B spectral intensities measured at three stations during 1992-1993, weighted by the measured absorption spectrum of DNA (shown at the left of the figure) [34]. The maximum intensity occurred at San Diego, California, on June 21, 1993, 10° Solar Zenith Angle; at Palmer in the Antarctic peninsula (64°S) on October 26, 1993, 52° SZA and at the South Pole on November 29, 1992, 68° SZA. The relative integrated intensities are South Pole, 0.11; San Diego, 0.59; Palmer 0.74.

the Antarctic can never be very large is no longer true. The question of possible biological damage associated with UV-B radiation then requires the separate assessment for each biological species of whether such damage is the result of cumulative UV-B exposure over an entire season or of a single, extremely intense exposure; both circumstances exist elsewhere.

CHANGING O₃ AND CFC CONCENTRATIONS IN THE 1990s

Ozone concentrations have continued to fall during the early 1990's. The measured value at the South Pole was only 91 D.U. on Oct. 12, 1993, and the vertical profile data from the corresponding balloon sonde indicated that all ozone had been removed from a 5 kilometer altitude band between 14 and 19 kilometers. The TOMS satellite registered many new daily record low global ozone values in early 1992, and then for nearly 13 months from mid-April, 1992, a new daily low global ozone value was measured (Figure 23). This measurement series ended when the TOMS instrument finally failed on May 7, 1993. The ozone data interpretations were complicated by the eruption of Mount Pinatubo in the Philippines in June 1991. This volcano, while not providing any significant amount of hydrogen chloride to the stratosphere, did introduce particulate surfaces on which could occur reactions

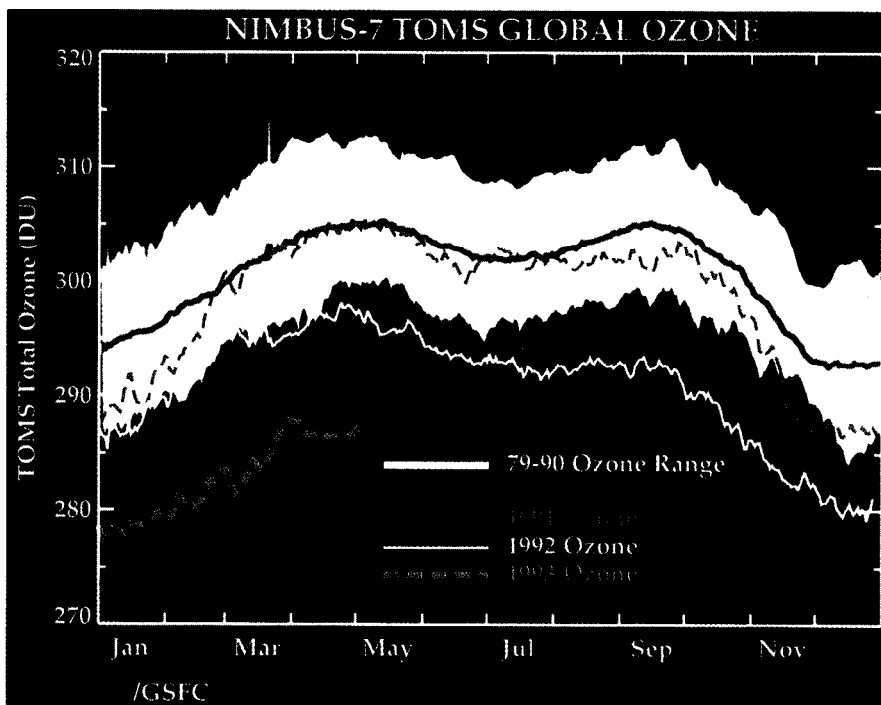


Figure (23) Global Ozone values as measured with the Total Ozone Mapping Spectrometer on the Nimbus 7 Satellite. The range of values recorded on each day from 1979-1990 is outlined in white, with the average for these years in red. The 1991, 1992, and 1993 values are shown in green, yellow and blue, respectively. The TOMS instrument failed on May 7, 1993.

similar to those taking place on the PSCs. The northern hemisphere Dobson stations continued to report declining ozone concentrations, with the losses now spreading into the summer. By 1995, the north temperate zone total ozone losses approached 10% during winter and spring and 5% in the summer and autumn [13].

In contrast, the measured tropospheric concentrations of the various halo carbon gases deviated in the 1990's from their earlier pattern of steady increases in response to the restrictions of the Montreal Protocol. The concentrations of the three major CFCs, which had risen almost linearly during the 1980's, markedly slowed this pace. By 1995, the concentrations of CCl_3F measured regularly at seven different stations varying in latitude from the polar Arctic to the South Pole had essentially leveled off, as shown in Figure 24. The CCl_2F_2 and $\text{CCl}_2\text{FCClF}_2$ concentrations were still rising, but at no more than half the rate of the 1980's. The sharpest changes were observed with the organic solvent methylchloroform, CH_3CCl_3 , for which controls were added in revisions of the original Montreal Protocol. Methylchloroform has three hydrogen atoms which are susceptible to attack by HO radicals in the troposphere, in analogy with reaction (1), and therefore have an average lifetime of only about 5 years. With its rapidly diminishing emission rate under the limitations of the Protocol, the tropospheric concentrations of CH_3CCl_3 reached a maximum in 1992, and have declined significantly since (Figure 24).

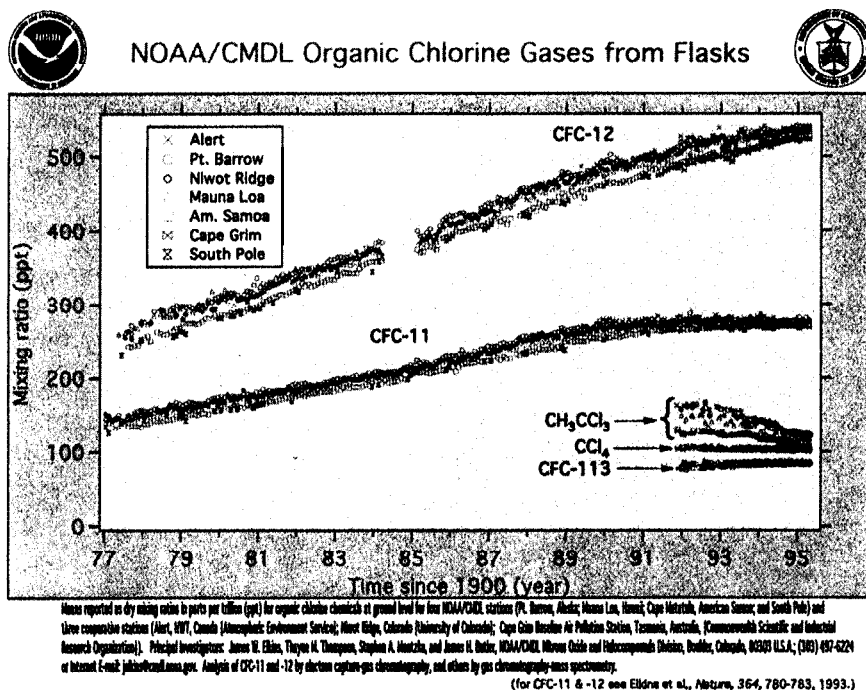


Figure (24) Measured Mixing Ratios in pptv, 1977–1995, for CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $\text{CCl}_2\text{FCClF}_2$ (CFC-113), CH_3CCl_3 and CCl_4 .

The situation at the end of 1995 is therefore a mixed one. The three most important CFC molecules have atmospheric lifetimes measured from many decades to a century or more, with the consequence that there will be significant quantities of them present in the atmosphere throughout the 21st century. The major springtime losses in the Antarctic will probably continue at least until mid-century. However, because the primary cause of these ozone losses are the man-made chlorine and bromine compounds limited by the Montreal Protocol, the amount of organochlorine in the troposphere will peak soon, if it hasn't already. When the weighted effects of bromine compounds are added in, the peak in tropospheric halocarbons will occur within this decade. Because of the delay time in rising upward, the stratospheric peak will follow within a few years. For the next few decades, the atmosphere will be loaded with chlorine and bromine compounds, so that a really large volcanic explosion with major increases in the particulate surface area of the stratosphere might cause transitory large ozone decreases. Another area for concern is the changing temperature structure of the stratosphere because of the steady increases in the greenhouse gases, especially carbon dioxide. The effect of more carbon dioxide is to decrease temperatures in the lower stratosphere, and this could lead to more extensive cloud formation, and more particulate surface area as well. However, with the limitations just expressed, the threat of extensive further stratospheric ozone depletion during the 21st century appears to be under control.

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